

Synthesis and characterization of new aramids based on *o*-(*m*-triphenyl)-terephthaloyl chloride and *m*-(*m*-triphenyl)-isophthaloyl chloride

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ABSTRACT

Two monomers *o*-(*m*-triphenyl)-terephthaloyl chloride (TPH1-COCl) and *m*-(*m*-triphenyl)-isophthaloyl chloride (TPH2-COCl) with bulky pendant groups were prepared, and they were polymerized with *p*-phenylenediamine (PPD) or copolymerized with PPD and terephthaloyl chloride (TPC) to prepare aromatic polyamides which were named TPH1 polymer and TPH2 polymer, respectively. The structures of the monomers with bulky pendant groups and the polymers were characterized by ¹H NMR and gel permeation chromatography. The resulting polymers are soluble in some organic solvents such as *N*-methyl-2-pyrrolidone. However, the solubility of the two series of polymers was different due to the different structures of the two monomers, and it is affected by the feeding ratio of the monomers. Both kinds of polymers have good thermal stabilities with 5% weight loss temperatures close to 500 °C. And glass transitions of some TPH2 polymers were observed. Most of these polyamides show lyotropic liquid crystalline (LLC) behaviors as evidenced by polarized light microscopy results. And the LLC properties are influenced by the structures, molecular weights, and concentrations of the polymers.

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1. Introduction

Aramid fibers are a class of high-performance polymeric materials, and they have been widely studied and used in military, transportation, and other fields [1–11]. Among them, poly(*p*-phenylene terephthalamide) (PPTA) is extensively researched and has realized its commercialization. Because of the strong hydrogen-bonding interaction and π - π stacking between the polymer chains, aramid fibers possess high thermal stability, low flammability, excellent chemical resistance, and excellent mechanical properties [12,13]. However, the high rigidity and strong interactions between PPTA chains result in a very high glass

transition temperature (T_g) and poor solubility in organic solvents [14]. PPTA is only soluble in solvents such as concentrated H₂SO₄ and forms a lyotropic liquid crystalline (LLC) phase [15,16]. It is well known that the liquid crystalline (LC) properties of the aramids in concentrated H₂SO₄ are very useful in the spinning process of these polymers [17]. However, H₂SO₄ is a highly corrosive solvent and an acid rain generator [18]. On the other hand, many expensive equipments must be applied in the manufacturing of aramid polymers due to the high cost of anti-corrosive materials. Furthermore, aramids often degrade in H₂SO₄ [17] and the molecular weights (MWs) and polydispersities of the polymers are difficult to be characterized. These drawbacks greatly limit the application of aramid polymers.

Many efforts have been made to improve the solubility of aromatic polyamides by preparing new chemical structures containing rigid aromatic backbones. Approaches such as introducing flexible functionalities [19–25], including alkyl side chains and main-chain ether linkages, and *N*-alkylation of the backbone are valuable in improving the solubility. However, the thermal stability of the

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polymers decreases [26,27]. Other methods include the introduction of bulky side substituents [28,29] and Y-shaped macromonomers [30–34]. The modified polymers have improved solubility and good thermal stability. Jian et al. [35,36] introduced twisted and non-coplanar structures into the backbone and then conducted a four-component copolymerization process to prepare aramid polymers. Some resulting polymers even exhibited LLC behaviors as evidenced by polarized light microscopy (PLM) results. However, the synthetic routes of the methods mentioned above are usually complex, and few aramids can exhibit LLC properties due to the disrupted structure of the rigid PPTA backbone.

The properties of aromatic polyamides are mostly influenced by the regularity and symmetry of the polymer structures. Herein, we design two monomers *o*-(*m*-triphenyl)-terephthaloyl chloride and *m*-(*m*-triphenyl)-isophthaloyl chloride with bulky pendants to prepare polyamides. Compared with the approach using Y-shaped monomers, our design strategy can maintain the rigidity of the polymer backbone to a great extent. The *m*-triphenyl unit has been proven to be thermally stable [30], while it can increase the distance between the polymer chains, thus improving the solubility. The chemical structures of polymers synthesized were characterized by ^1H NMR and gel permeation chromatography (GPC). The solubility was also examined. And thermal properties were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The LLC properties were investigated by PLM.

2. Experimental

2.1. Materials

1-Bromo-3,5-diphenylbenzene (95%) was purchased from Bide Pharmatech Co., Ltd. 2,5-Dimethylphenylboronic acid (C.R.) and 3,5-dimethylphenylboronic acid (C.R.) were purchased from Beijing Ouhe Technology Co., Ltd. *p*-Phenylenediamine (PPD, 99%) and terephthaloyl chloride (TPC, 99.5%) were purchased from J&K. $\text{Pd}(\text{PPh}_3)_4$ (99%) was purchased from Energy Chemical Co., Ltd. *N*-Methy-2-pyrrolidone (HPLC) was purchased from Aladdin Industrial Co., Ltd. PPTA resin was supplied by Yantai Tayho Advanced Materials Co., Ltd., and its inherent viscosity is 3.4 dL/g. SOCl_2 , LiCl, tetrahydrofuran (THF), K_2CO_3 , *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc),

$\text{CH}_3\text{CH}_2\text{Br}$, NaH, and other reagents were purchased from Beijing Chemical Reagents.

2.2. Characterization methods

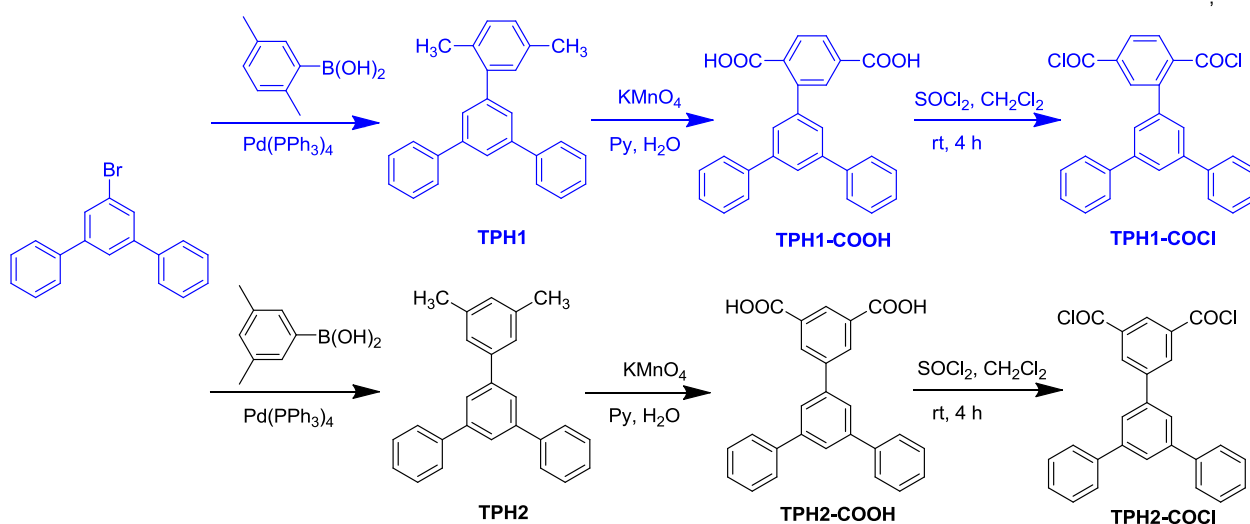
^1H NMR spectra were recorded at 400 MHz on a Bruker ARX 400 spectrometer. Mass spectra were recorded on a Finnigan-MAT ZAB-MS. GPC measurements were performed on a Waters 2414 instrument consisting of a Waters 2414 refractive index (RI) detector and a Waters 1515 pump. DMF-LiCl was used as eluent at a flow rate of 1 mL/min at 50 °C. Poly(methyl methacrylate)s (PMMA)s were used as standards. TGA was conducted on a TA Q600 SDT instrument in nitrogen or air at a heating rate of 20 °C/min. The flow rate was 100 mL/min. DSC experiments were performed on a TA DSC Q100 instrument during the second heating process under nitrogen, with a heating rate of 20 °C/min and a flow rate of 50 mL/min. PLM was performed on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage.

2.3. Synthesis

The synthetic route of the two monomers with bulky pendants is shown in Scheme 1. The details are described below, with the synthesis of the TPH2 polymer as an example.

2.3.1. Synthesis of 3,5-dimethyl-5'-phenyl-1,1':3',1''-terphenyl (TPH2)

1-Bromo-3,5-diphenylbenzene (5.600 g, 18.18 mmol), 3,5-dimethylphenylboronic acid (4.050 g, 27.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (2.090 g, 1.808 mmol), and K_2CO_3 (6.050 g, 43.84 mmol) were charged into a three-necked round-bottomed flask which was vacuumed and purged with nitrogen. Then THF/H₂O (160 mL/120 mL) was added under nitrogen. The solution was stirred at 90 °C for 48 h before it was quenched with 1 M HCl. The reaction mixture was washed by water, extracted with CH_2Cl_2 , and then dried. The final product was passed through a silica gel column using dichloromethane/petroleum ether (1/3, v/v) as the eluent. Yield: 86%. Synthesis of TPH1 with the similar method is described in Supplementary Content, with a yield of 94%. ^1H NMR for TPH2 (400 MHz, DMSO, δ , ppm): 2.37 (s, 6H), 7.04 (s, 1H), 7.40–7.44 (t, $J = 7.2$ Hz, 2H), 7.48–7.53 (q, $J = 7.9$ Hz, 6H), 7.85–7.87 (m, 7H). HRMS (EI): calcd. (M)/z, 334.17; found (M)/z, 334.2. EA: calcd. for



Scheme 1. Synthetic route of the monomers with bulky pendants.

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